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THREE-DIMENSIONAL PHOTOCHEMICAL MACHINING WITH LASERS  
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FIRST SEMI-ANNUAL TECHNICAL REPORT

on

THREE-DIMENSIONAL PHOTOCHEMICAL  
MACHINING WITH LASERS

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

December 5, 1983

Sponsored by

Advanced Research Projects Agency (DOD)  
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## REPORT SUMMARY

Research on the development of new photoinitiator systems for spatially selective three-dimensional photochemical machining with lasers has continued smoothly and is progressing well. A number of promising new candidate materials have been identified, including a rubrene sulfonyl chloride derivative and several brominated porphyrin derivatives, and these are now being evaluated experimentally. In addition, detailed calculations of materials properties and optical parameters have been carried out to help guide the experimental effort.

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FIRST SEMI-ANNUAL TECHNICAL REPORT

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THREE-DIMENSIONAL PHOTOCHEMICAL  
MACHINING WITH LASERS

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

from

BATTELLE

Columbus Laboratories

December 5, 1983

INTRODUCTION

This document represents Battelle's First Semi-Annual Technical Report to the Air Force Office of Scientific Research on Three- Dimensional Photochemical Machining With Lasers, under Contract No.

F49620-82-C-0077, for the period August 1, 1982 through January 31, 1983. (Please note that, although the contract effective date is June 1, 1982, delays in the receipt of a signed contract resulted in an actual start date of August 1, 1982 for the research effort; thus, this report covers the first six months of the actual research effort, as provided in the description of reporting periods in the subject contract.)

Our research efforts during this reporting period have focused on identifying and acquiring candidate materials which offer the promise of providing selective photopolymerization when irradiated simultaneously with two laser beams of different colors, but of being inert to the presence of either beam alone. Such materials are crucial to the success of this program, for without this degree of control it will be impossible to construct three-dimensional objects photochemically. Our strategy has

been to seek materials containing a free-radical initiating group (such as an easily cleaved halogen atom, for example) which can be broken apart with high-energy ultraviolet photons. Spatially selective photopolymerization can then be obtained, at least in principle, if an initiator moiety of this type is attached to a molecule whose spectroscopy shows that (a) normal singlet-singlet absorption occurs with visible light of energies below the dissociation threshold of the initiator group, and (b) intersystem crossing occurs rapidly and efficiently to produce a metastable triplet excited state which can subsequently be excited above the dissociation threshold by a second photon of visible or near-infrared light.

Our efforts to date have resulted in the identification and acquisition of several such materials, including a derivative of rubrene dibromide, and two new brominated porphyrin derivatives. These materials all have labile bromine atoms which are expected to cleave with UV irradiation, and we have already confirmed that methyl methacrylate can be polymerized when the porphyrin system is irradiated both with green (514 nm) light from an argon ion laser and in two-photon experiments with red and nearIR light. Further, we have confirmed that methyl methacrylate can be polymerized selectively when naphthalene sulfonyl chloride (a known UV-sensitive photoinitiator) is irradiated with visible light in the presence of 9,10-dibromoanthracene, which absorbs the light and intersystem crosses rapidly to its second excited triplet state. While this state has a lifetime of only a few nanoseconds, it can still be trapped by the naphthalene sulfonyl chloride, demonstrating that upper triplets can indeed sensitize photopolymerization.

We have also synthesized a sulfonyl chloride derivative of rubrene which appears promising. The sulfonyl chloride group is known to be a good photoinitiator for MMA, and it has the virtue of being photoactive regardless of its specific site of attachment to the rubrene molecule. Samples of this material are now being purified for analysis and evaluation.

Finally, a series of detailed calculations have been carried out to help define the materials properties and optical parameters that will be required for a PCM system to operate effectively. We find that it is important to have at least  $10^3$  polymer crosslinks per photoinitiator molecule -- a reasonable number -- and that one of the principal tradeoffs is between resolution (the number of points addressed for an object of a given volume) and the time required to form the object. Given modest laser powers and reasonable kinetics, it seems that an object as large as 10 cm x 10 cm x 10 cm could be fabricated with 10  $\mu$ m resolution in a period of a few days. This contrasts with the time of several months often required for fabrication by conventional techniques. One outgrowth of this work has been the conception of an innovative new design for rapidly changing the focal point of a laser beam, a key feature in the ultimate realization of the PCM technique. In short, work is continuing to progress well in all aspects of the program.

No major items of experimental or special equipment were purchased or constructed during this reporting period, and no travel or visits were made during the reporting period. No major problems or deviations from the program plan have been encountered to date.



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